CHAPTER II
LITERATURE SURVEY

2.1 Electrorheological (ER) Fluids

Electrorheological (ER) suspensions, first studied extensively by Winslow (1949), display dramatic changes in rheological properties under a sufficiently large electric field (Klingenberg, 1993). A typical ER fluid is a suspension of micron-sized polarizable particles dispersed in a non-conducting medium. The mismatches in conductivity and dielectric permittivity between the dispersed particles and the continuous medium induce dipolar polarization in the particles upon application of an electric field. Under the action of the field, the induced dipoles tend to attract neighboring particles and this causes the particles to form fibrillar three dimensional network structures, which are aligned along the direction of the electric field and generate additional resistance against fluid motion (Tao and Sun, 1991, Lee *et al.*, 1998). The time scale for this transition is of the order of milliseconds (Klingenberg *et al.*, 1993). Because of the controllable viscosity and the fast response, ER fluids are regarded as smart materials with potential for application in active devices which transform electric energy to mechanical energy (Choi *et al.*, 1998). Possible applications include clutches, breaks, shock absorbers, engine mounts, valves, flow pumps, and other variable control and servo devices (Jang *et al.*, 2001).

2.2 Force Relevant to Electrorheology

Several different interparticle forces are included in microscopic models of ER in which they have commonly used to describe and interpret suspension behavior (Parthasarathy and Klingenberg, 1996).

2.2.1 Electrostatic Forces

Determining the electrostatic forces on particles in ER suspensions requires solving for the electrostatic potential field within the ER system, which are heterogeneous, consisting of particles and oil, often accompanied by activators, stabilizers, and ionic impurities. The particles are usually non-spherical, irregular and often porous. Within this complicated system, the electrostatic potential is influenced by a variety of phenomena: multiple modes of polarization, nonuniform charge distributions and the formation of electric double layers, nonlinear dielectric phenomena, and the likelihood of electrochemistry. Calculation of electrostatic forces has thus understandably evolved from simplified physical models; Idealized electrostatic polarization model (where both point-dipole approximatation and multipole-multibody effects are considered), Maxwell-Wagner polarization, and Nonlinear conduction.

2.2.2 Hydrodynamic Forces

Particles in ER suspensions are much larger than the molecules comprising the continuous phase, and thus the fluid phase is typically treated as a continuum. The particles are still sufficiently small, and the continuous phase sufficiently viscous, so that the particle Reynolds number is usually small. Thus, hydrodynamic interactions between particles, as well as between particles and the bounding electrodes, are often ignored in models of ER, in which case the force on a spherical particle simplifies to Stokes' drag. Rotational motions are typically ignored. These simplifications are likely to introduce significant errors when hydrodynamic forces begin to dominate over other forces acting on the particles.

2.2.3 Brownian Forces

The fluid phase can also influence particle dynamics via Brownian motion. The thermal motion of the continuous phase molecules results in constant bombardments on a disperse phase particle, which alters the particle's momentum.

2.2.4 Short-range Repulsion

Short-range repulsive forces acting between ER particles, arising from such phenomena as Born repulsion, solvation farces, or steric interactions, will act over distances ranging from Angstroms to nanometers.

2.2.5 Other Colloidal Forces

The van der Waals interaction is most likely to be of concern in ER suspensions, as compared to DLVO-type electrostatic repulsion, where aggregation can compromise stability and lead to a yield stress even in the absence of an external electric field.

2.2.6 Adhesion due to Water Bridges

In addition to its impact on disperse and continuous phase electrical properties, water may influence ER behavior by forming bridges between particles near contact. This force does not depend on asperity size, but does depend on the particle size, and varies linearly with the electric field strength.

2.2.7 Dimensionless Groups

The structure and rheology of ER suspensions are determined by the competition between all of the forces described above, and perhaps others. Various dimensionless groups have been employed to describe the relative importance of competing contributions, and to analyze and interpret results. For steady shear flow, the relative importance of hydrodynamic to electrostatic polarization forces is described by the Mason number,

$$Mn = \frac{\eta_c \gamma^{\circ}}{2\varepsilon_0 \varepsilon_c \beta^2 E_0^2}$$

The relative importance of hydrodynamic to thermal forces is described by the Peclet number,

$$Pe = \frac{3\pi a^3 \eta_c \gamma^{\circ}}{kT}$$

and the relative magnitude of electrostatic to thermal contributions is described by the parameter λ,

$$\lambda = \frac{\pi \varepsilon_0 \varepsilon_c a^3 \beta^2 E_0^2}{2kT}$$

2.3 ER Particle Materials

When formulating an ER fluid for a specific application, the requirements of a good ER fluid are the following (Goodwin *et al.*, 1997):

i. There should be a large change in rheological properties on the application of electric field.

ii. The off-field viscosity should be close to that of the oil phase and insensitive to temperature.

iii. The current requirement should be low to minimize power loss as well as heating effects.

iv. Low temperature sensitivity and hence water-free systems have an advantage.

v. There should be tenability of the particle properties to enable the maximum control of ER properties as well as the suspension stability properties to be achieved.

vi. There should be a strong effect in both DC and AC fields.

vii. For comparison with theoretical models, monodisperse spherical particles would be the system of choice.

A wide variety of particulate materials of different chemical nature have been employed in ER fluids. For simplicity, research in ER particulates is classified in two general categories of materials: extrinsically polarizable and intrinsically polarizable.

2.3.1 Extrinsically Polarizable Materials

Extrinsically polarizable ER fluids are composed of hydrophilic particles that require water or some other polar activator to obtain measurable ER activity. The amount of water required in optimizing the ER effect depends on the physical and chemical properties of the particles as well as the desired ER properties. Although extrinsically polarizable ER fluids are able to demonstrate the ER phenomenon, they have significantly limitations in application (e.g. thermal stability). At extreme temperatures, the polar activator may not be available to activate the ER fluid, for example, because of the activator's freezing and boiling points and because the partitioning of the activator between the various phases tends to change with temperature. Examples of these materials include zeolite, lead zirconate titanate, cellulose, silica, aluminar, and starch particles.

2.3.2 Intrinsically Polarizable Materials

The discovery that a polar activator is not necessary to obtain ER activity catalyzed resurgence of interest in electrorheology (Cho and Choi, 2000). The advantages of intrinsically polarizable materials include a simple system, thermal stability, and conductivity controllable. Example of these materials, include metal particles, conductive or semi-conductive polymers. Recently, there has been interest in using conductive polymers as suspended particles for dry-base ER fluids. Conductive polymers can offer a variety of advantages for ER systems: better thermal stability, insolubility, and more controllable viscosity. Suspensions of conductive polymers exhibit intrinsic ER properties without the necessity to introduce other additives. The polarization is induced by the motion of electrons within the suspended particles under application of electric field. Various conductive polymers have been tested as particulate materials in ER systems. Examples include polyaniline (PANI) and many PANI derivatives, based upon modification of oxidation state, dopant, and polymerization conditions (Lee *et al.*, 1998, Choi *et al.*, 1998, Jang *et al.*, 2001, Gow and Zukoski, 2000, Gozdalik et al., 2000, Akhavan and Slack, 2001, Kim *et al.*, 2000, Lee *et al.*, 2001, Lengalova *et al.*, 2003, Cho *et al.*, 2004), polythiophene(Chotpattananont *et al.*, 2003, 2004), and polyparaphenylene (Sim *et al.*, 2001, Chin *et al.*, 1998).

2.4 Literature survey

Electrorheological phenomenon was discovered in 1949; W.M. Winslow (1949) demonstrated that certain dispersions composed of finely divided solids dispersed in a non-conducting liquid showed the electrorheological behavior. These materials showed a very marked increase in flow resistance when exposed to electric field of 4 kV/mm and they were called as ‘electroviscose fluids’ to describe his materials (Winslow, 1949).

The conductive polymeric particles have been widely developed as ER materials for dry-base such as polyaniline, poly(p-phenylene), polypyrrole, and polythiophene. Among them, polyaniline and is derivatives are widely investigated.

Gow and Zukoski (1989) studied electrorheological suspension of polyaniline suspension under steady and transient shear modes and found that static yield stress of the suspensions increased with increasing particle conductivity, particle concentration. However, particles with conductivity greater than 10^{-7} could not be effectively used as ER particles because of severe current leakage. The suspension viscosity was found to increase 10^{6}-10^{8} Pa s. At field greater than a critical electric field strength, E*, the suspensions took on solid like behavior which could support stress under creep experiment. Moreover, polyaniline particles were found to form flocculate structures where the agglomerate strength was independent of doping level (Gow and Zukoski, 1990). *Choi et al.* (1998) investigated suspension of polyaniline in silicone oil s a potential candidates for dry-base ER systems. The steady shear experiments were conducted to investigate the effect of imposed electric fields and particle conductivity. ER performance of this fluid found to be improved by increasing both electric field strength and the conductivity of the polyaniline particles. Moreover, the shear stress of this fluid at different applied electric fields could be scaled into the universal curve by the dynamic yield stress which increased linearly with the square of the electric field strength. Various types of dopants were used to adjust the particle conductivity of conductive polymers (Choi *et al.*, 1998). Kim *et al.* (2000) investigated the effects of electric field strength and particle concentration on the ER properties of dodecylbenzene sulfonic acid (DBSA) doped polyaniline suspensions in silicone oil. Similar to many other ER fluids, this suspension also possessed the properties that yield stress increased as particle concentration increase (Kim *et al.*, 2000). The camphorsulfonic acid (CSA) doped polyaniline base ER fluids were investigated by Jang *et al.* (2001). The ER response of this system increased with electric field strength and showed the best electrical stability in the region of pH 10. They proposed that the electron movement within the PANI-CSA particles and electron hopping between the PANI-CSA particles play the important role in the surface polarization, the yield stress increases. Cho *et al.* (2004) studied viscoelastic properties by using applied electric fields using a rotational rheometer. Within the linear viscoelastic region, the ER fluid was observed to be elastic, due to columnar structure of PANI particles sustaining the deformation. Its rheological functions (G' and G") were interpreted based on the dimensional analysis, and they showed roughly linear electric-field dependence. Furthermore, the recovery percentage obtained from the creep and recovery experiments increased with applied electric fields (Cho *et al.*, 2004). Under oscillartory shearing flow, Chin and Winter (2002) found that G’ and G” grew by orders of magnitude and showed gelation pattern of network polymer under action of electric field. At the gel point, the slow dynamics is governed by power-law relaxation behavior (frequency dependent tanδ). The gel point was found at low field strength where the percolating structure was very fragile (Chin and Winter, 2002).

Electromechanical response of poly(dimetylsiloxane) (PDMS) dielectric gel was investigated by Bohon and Krause (2001). The samples were cured between two flexible electrodes and the displacement of the electrodes when an electric field was applied was observed by using an optical microscope. The pure PDMS gel showed small response compared to that of PDMS gel blended with an electrorheological fluids and the composite gel displacement was greatest using 60/40 PDMS/ERF combination. Krause and Bohon (2001) studied the electromechanical response of polymeric gels. The samples were prepared by curing of electrorheological fluids, PANI particles suspended in PDMS fluids, in the matrices of cross-linked PDMS networks (XPDMS). The response of composite gel systems was found to be fast, occurring in ~100ms, depending on the compression modulus of the matrices. For composite gel in which PANI particles were prealigned under electric field during curing, it showed the higher compression modulus than the gel containing random PANI particles by an order of magnitude. Feher et al. (2001) prepared a new type of soft actuator by blending TiO_2 particles in weakly crosslinked PDMS gels and fabricating the gel into cylinder. The gel was then immersed into silicone oil in order to attain the swelling equilibrium. High DC voltage was applied in a non-contact mode through electrodes and the electric response of the gel was recorded by a video camera. They found that the filler-loaded gel cylinder, suspended in silicone oil showed significant and rapid bending, when en external electric field was applied. The bending behavior was found to be reversible and always occurred towards the cathode.

2.5 Objective and scope of work

Our objective for this dissertation is to develop high-performance soft and flexible actuator from anhydrous conductive polyaniline particles. In this research work, the polyaniline, PANI/PDMS composites were studied as electrotheological fluids and electroviscoelastic material. We have studied the rheological properties of these composites under the application of DC electric field. Since electrorheological fluid is operated in both dynamic and steady conditions in the actual applications, the ER materials should be able to maintain the ER characteristic under either condition. Therefore, the investigation of ER properties is done in both dynamic, i.e., oscillatory and steady shear conditions.

In chapter IV of this dissertation, properties of the PANI/silicone oil suspension is investigated under oscillatory shear flow. The dynamic moduli, storage (G') and loss (G"), are measured. The effects of electric field strength, particle concentration, and host fluid viscosity are reported. The static yield strength τ_y, of the formation structure as well as the residual that remains after electric field removal are also studied. A viscoelastic liquid to solid transition can be observed at a critical electric field strength in this chapter where more details and dimensionless parameters the Mason number (Mn), varies with Peclet number (Pe) of the system are further investigated in chapter V. The creep response of the suspensions and how it depends on electric field strength, particle concentration, and operating temperature are studied in chapter VI. Finally, electroviscoelastic behaviors of camphorsulfonic acid (CSA) – doped polyaniline (PANI) particles embedded in an elastic cross-linked PDMS matrix are investigated in chapter VII.